(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 016 706 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
05.07.2000 Bulletin 2000/27

(21) Application number: 99310591.5

(22) Date of filing: 24.12.1999

(51) Int. Cl.[7]: C10M 163/00
// (C10M163/00, 129:10, 129:54, 129:76, 133:56, 137:10, 159:22, 159:24), C10N30:04, C10N30:10, C10N40:25

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 28.12.1998 JP 37312298

(71) Applicant: ORONITE JAPAN LIMITED
Minatu-ku, Tokyo (JP)

(72) Inventors:
, Nagamatsu, Horoyuki
Gotenba-shi, Shizuoka (JP)
, Fujita, Koichi
Haibara-gun, Shizuoka (JP)
, Ando, Hiroki
Haibara-gun, Shizuoka (JP)

(74) Representative:
Nash, David Allan
Haseltine Lake & Co.,
Imperial House, 15-19 Kingsway
London WC2B 6UD (GB)

(54) **Lubricating oil composition for internal combustion engines having improved thermal oxidation durability and detergency**

(57) A lubricating oil composition for internal combustion engines comprising a base oil of lubricating viscosity having a kinematic viscosity of 22 to 300 mm^2/s at 40°C, an overbased alkyloxybenzenesulfonate detergent, a neutral or basic salicylate detergent, an ashless dispersant, a zinc dialkyldithiophosphate, and a nonmetallic oxidation inhibitor.

The lubricating oil composition of the present invention has enough stability against thermal oxidation and enough detergency at elevated temperatures to comply with the severe operating conditions required for modern diesel engines and to satisfactorily lubricate the engine even under severe friction conditions.

Description

The present invention relates to a lubricating oil composition favorably employable for internal combustion engines, particularly trunk piston engines such as land generators and ships. The lubricating oil composition of the present invention provides improved thermal oxidation durability and detergency when used to lubricate an internal combustion engine.

BACKGROUND OF THE INVENTION

Lubricating oils for internal combustion engines are formulated from a range of base fluids and chemical additives. The base fluid has several functions but primarily it is the lubricant, providing a fluid layer separating moving surfaces or removing heat and wear particles while keeping friction at a minimum. Many of the properties of lubricating oils are enhanced or created by the addition of special chemical additives in the base fluid.

Modern sophisticated complex machinery demands much more from all lubricating oils. Intricate engines with close tolerances between moving parts would not be possible without engine oils containing a tailored package of chemical additives. Progressive advances in additive technology not only allow today's engines to operate efficiently, but also dramatically increase the engine's useful life and reduce engine maintenance costs. Detergents and dispersants have a vital role in formulating engine-lubricating oils. The principle functions performed by detergents in lubricating oil formulations are (1) acid neutralization, (2) high temperature detergency, (3) oxidation inhibition and (4) rust prevention. These functions provide engine cleanliness and extended trouble-free operation. Dispersants supplement these functions and, in addition, provide against low-temperature sludge deposits.

According to Japanese Patent Provisional Publication No. H95-11015 (equivalent to PCT WO 96/20265, published July 1, 1996), a metal-containing detergent of an overbased alkyloxybenzenesulfonate has high detergency and can be obtained at a relatively low cost. Examples of the additive compositions containing an overbased alkyloxybenzenesulfonate employed for additive compositions of lubricating oils for marine diesel engines are presented in the reference. Those examples include the compositions containing: a combination of an overbased alkyloxybenzenesulfonate (e.g., overbased phenoxysulfonate) and a zinc dialkyldithiophosphate (ZnDTP); a combination of an overbased phenoxysulfonate and an alkenylsuccinimide ashless dispersant; a combination of an overbased phenoxysulfonate, ZnDTP and an ashless dispersant; a combination of an overbased phenoxysulfonate and a nonmetallic oxidation inhibitor such as phenolic oxidation inhibitor and an alkylated diphenylamine oxidation inhibitor; a combination of an overbased phenoxysulfonate, ZnDTP and a nonmetallic oxidation inhibitor; a combination of an overbased phenoxysulfonate, an ashless dispersant, ZnDTP and/or a nonmetallic oxidation inhibitor; a combination of an overbased phenoxysulfonate and an overbased sulfide of alkylphenate or alkylsalicylate; a combination of an overbased phenoxysulfonate, an overbased sulfonate and ZnDTP; a combination of an overbased phenoxysulfonate, an overbased phenate sulfide and an ashless dispersant; a combination of an overbased phenoxysulfonate, an overbased phenate sulfide, an ashless dispersant and ZnDTP; and a combination of an overbased phenoxysulfonate, an overbased alkylphenate sulfide, ZnDTP, an ashless dispersant and a nonmetallic oxidation inhibitor.

While the detergent-dispersant combinations taught by the above Japanese Patent Provisional Publication No. H95-11015 are useful lubricating oil formulations; they prove to be inadequate in satisfying the lubricating requirements of internal combustion engines, particularly trunk piston engines such as land generators and ships. The operation of these types of internal combustion engines places a higher demand on thermal oxidation durability and detergency, particularly at elevated temperatures, which the detergent-dispersant compositions of the above Japanese Patent Provisional Publication No. H95-11015 does not provide. With the demand for longer drain intervals, the need to control thermal oxidation durability and detergency becomes more important.

Accordingly, it is an object of the present invention to provide a lubricating oil composition which is satisfactorily employable under the severe operating conditions typically observed with internal combustion engines operated at elevated temperatures, particularly trunk piston engines such as land generators and ships. The lubricating oil composition provided by the present invention has enough stability against thermal oxidation and enough detergency to satisfactorily lubricate the engine at an elevated temperature.

SUMMARY OF THE INVENTION

The present invention relates to a lubricating oil composition having improved thermal oxidation durability and detergency for internal combustion engines, particularly trunk piston engines such as land generators and ships. The improvement is particularly noticeable at elevated temperatures. The lubricating oil composition of the present invention comprises the product produced by blending:

(A) a base oil of lubricating viscosity having a kinematic viscosity of 22 to 300 mm^2à/s at 40°C,

(B) 1.0 to 20.0 wt. % of an overbased alkyloxybenzenesulfonate detergent,

(C) 1.0 to 20.0 wt. % of a neutral or basic salicylate detergent,

(D) 0.1 to 10.0 wt. % of an ashless dispersant,

(E) 0.1 to 2.0 wt. % of a zinc dialkyldithiophosphate, and

(F) 0.05 to 2.0 wt. % of a nonmetallic oxidation inhibitor.

In one embodiment, the present invention relates to a lubricating oil composition for internal combustion engines comprising the product produced by blending:

(A) a base oil of lubricating viscosity having a kinematic viscosity of 22 to 300 mm^2/s at 40°C,

(B) 0.1 to 2.5 wt. % in terms of calcium content of an overbased calcium alkyloxybenzenesulfonate detergent,

(C) 0.05 to 2.0 wt. % in terms of calcium content of a neutral or basic calcium salicylate detergent,

(D) 0.001 to 0.15 wt. % in terms of nitrogen content of an ashless succinimide dispersant,

(E) 0.001 to 0.15 wt. % in terms of phosphorus content of a zinc dialkyldithiophosphate, and

(F) 0.05 to 2.0 wt. % in terms of content of its phenolic oxidation inhibitor.

In another embodiment, the present invention further relates to a concentrate comprising the product produced by blending:

(A) 1.0 to 30 wt. % of a compatible organic liquid diluent,

(B) 5.0 to 90.0 wt. % of an overbased alkyloxybenzenesulfonate detergent,

(C) 5.0 to 90.0 wt. % of a neutral or basic salicylate detergent,

(D) 0.5 to 50.0 wt. % of an ashless dispersant.

(E) 0.5 to 15.0 wt. % of a zinc dialkyldithiophosphate, and

(F) 0.1 to 15.0 wt. % of a nonmetallic oxidation inhibitor.

The present invention further relates to a concentrate comprising the product produced by blending:

(A) 1.0 to 30 wt. % of a compatible organic liquid diluent,

(B) 0.5 to 12.0 wt. % in terms of calcium content of an overbased calcium alkyloxybenzenesulfonate detergent,

(C) 0.3 to 10.0 wt. % in terms of calcium content of a neutral or basic calcium salicylate detergent,

(D) 0.005 to 1.0 wt. % in terms of nitrogen content of an ashless succinimide dispersant,

(E) 0.005 to 1.1 wt. % in terms of phosphorus content of a zinc dialkyldithiophosphate, and

(F) 0.1 to 15.0 wt. % in terms of content of its phenolic oxidation inhibitor.

In still another embodiment, the present invention relates to a method of improving the thermal oxidation durability and detergency of an internal combustion engine by lubricating the internal combustion engine with the lubricating oil composition of the present invention.

In yet another embodiment, the present invention further provides a method of producing a lubricating oil composition by blending a mixture of:

(A) a base oil of lubricating viscosity having a kinematic viscosity of 22 to 300 mm^2/s at 40°C,

(B) 1.0 to 20.0 wt. % of an overbased alkyloxybenzenesulfonate detergent,

(C) 1.0 to 20.0 wt. % of a neutral or basic salicylate detergent,

(D) 0.1 to 10.0 wt. % of an ashless dispersant,

(E) 0.1 to 2.0 wt. % of a zinc dialkyldithiophosphate, and

(F) 0.05 to 2.0 wt. % of a nonmetallic oxidation inhibitor.

Among other factors, the present invention is based upon the unexpected discovery that the thermal oxidation durability and detergency in an internal combustion engine can be improved by lubricating such an engine with the lubricating oil composition of the present invention. The lubricating oil composition of the present invention has enough stability against thermal oxidation and enough detergency at an elevated temperature to comply with the severe operating conditions for diesel engines, particularly trunk piston engines such as land generators and ships.

DETAILED DESCRIPTION OF THE INVENTION

As mentioned above, the present invention relates to a lubricating oil composition that improves the thermal oxidation durability and detergency in internal combustion engines. Prior to discussing the present in further detail, the following terms will be defined.

By "TAN", we mean "Total Acid Number", which refers to the amount of acid equivalent to milligrams of KOH in one gram of additive. TAN can be determined by the procedure described in ASTM D 664 or any other equivalent procedure.

By "TBN", we mean "Total Base Number", which refers to the amount of base equivalent to one milligram of KOH in one gram of additive. Thus, higher TBN numbers reflect more alkaline products and therefore a greater alkalinity reserve. The Total Base Number for an additive composition is readily determined by ASTM test method D2896 or other equivalent methods.

By "internal olefins", we mean an olefin wherein the double bond is at other than the 1-, 2-, or 3- position of the alkene.

Base Oil of Lubricating Viscosity

The base oil of lubricating viscosity used in the present invention may be mineral oils or synthetic oils of viscosity suitable for use in the crankcase of an internal combustion engine such as gasoline engines and diesel engine which include marine engines. Crankcase lubricating oils ordinarily have a kinematic viscosity of 22 to 300 mm^2/s at 40°C, preferably 22 to 140 mm^2/s at 40°C.

The lubricating base oils may be derived from synthetic or natural sources. Mineral oils for use as the base oil in this invention include paraffinic, naphthenic and other oils that are ordinarily used in lubricating oil compositions and can be obtained from crude oil by distillation (under atmospheric or reduced pressure) and purification (e.g., solvent extraction, hydrocracking, solvent dewaxing, hydrogenation refining).

Synthetic oils include both hydrocarbon synthetic oils and synthetic esters. Useful synthetic hydrocarbon oils include liquid polymers of alpha olefins having the proper viscosity. Especially useful are the hydrogenated liquid oligomers of C_6 to C_{12} alpha olefins such as 1-decene trimer. Likewise, alkyl benzenes of proper viscosity, such as didodecyl benzene, can be used. Useful synthetic esters include the esters of monocarboxylic acids and polycarboxylic acids, as well as monohydroxy alkanols and polyols. Typical examples are didodecyl adipate, pentaerythritol tetracaproate, di-2-ethylhexyl adipate, dilaurylsebacate, and the like. Complex esters prepared from mixtures of mono- and dicarboxylic acids and mono- and dihydroxy alkanols can also be used. Blends of mineral oils with synthetic oils are also useful.

Overbased Alkyloxybenzenesulfonate Detergent

An overbased alkyloxybenzenesulfonate detergent is incorporated in an amount of 1.0 to 20.0 wt. %, preferably 2.0 to 10.0 wt. %, and most preferably 4.0 to 8.0 wt. %, based on the total amount of the lubricating oil composition of the present invention. Generally in the detergent, a hydrocarbon oil, which has been used in preparing the overbased alkyloxybenzenesulfonate, is contained in a small amount, and hence the above-mentioned amount for the detergent

includes not only the active component but also the remaining hydrocarbon oil. In the case where an overbased calcium alkyloxybenzenesulfonate is used as the detergent, the amount of the overbased calcium alkyloxybenzenesulfonate may be 0.1 to 2.5 wt. %, preferably 0.25 to 1.26 wt. %, in terms of the calcium content.

The overbased alkyloxybenzenesulfonate detergent can be prepared by the process described in the above Japanese Patent Provisional Publication No. H95-11015, the disclosure of which is hereby incorporated by reference. The process comprises the steps of alkylating hydroxybenzene with an olefin having an internal olefin in an amount of 40 to 80 wt. % to give an alkyloxybenzene, sulfonating and neutralizing the alkyloxybenzene, and converting the obtained compound into an overbased form. Preferably, the detergent is a calcium salt of an overbased alkyloxybenzenesulfonic acid (i.e., overbased calcium alkyloxybenzenesulfonate) having a TBN (Total Base Number as defined by D2896) of at least 200, preferably at least 250 (mg KOH/g).

If the content of the overbased alkyloxybenzenesulfonate detergent in the lubricating oil composition is less than 1.0 wt. %, the oil composition cannot have enough thermal oxidation durability and detergency to prevent its viscosity increase. On the other hand, if the detergent is incorporated in an amount of more than 20.0 wt. %, the improved thermal oxidation durability and detergency corresponding to the increased amount are not expected. The use of the overbased alkyloxybenzenesulfonate detergent in such a large amount is not economical.

Salicylate Detergent

Further, a neutral or basic salicylate detergent is also incorporated into the lubricating oil composition in an amount of 1.0 to 20.0 wt. %, preferably 1.0 to 10.0 wt. %, and most preferably 2.0 to 8.0 wt %, based on the total amount of the lubricating oil composition of the present invention. Generally in the detergent, a hydrocarbon oil, which has been used in preparing the salicylate, is contained in a small amount, and hence the above-mentioned amount for the detergent includes not only the active component but also the remaining hydrocarbon oil. In the case where calcium salicylate is used as the detergent, the amount of calcium salicylate detergent may be 0.05 to 2.0 wt. %, preferably 0.06 to 1.0 wt. %, in terms of the calcium content.

The neutral or basic salicylate detergent can be prepared in a manner apparent to one skilled in the art, for example, from salicylic acid having a hydrocarbyl group such as an alkyl group of 12 to 30 carbon atoms. Examples of the salicylate detergents include alkaline earth metal (e.g., calcium, magnesium) salts of salicylic acid derivatives having hydrocarbyl groups. In addition to those, various mixtures (e.g., a mixture of salicylate and phenate) are also employable. Preferred is an overbased calcium salicylate having a TBN of 60, preferably at least 100, more preferably at least 150, most preferably at least 200.

If the content of the salicylate detergent in the lubricating oil composition is less than 1.0 wt. %, the composition can not have enough thermal oxidation durability and detergency to prevent its hydrolysis, and the TBN value is liable to decrease. On the other hand, even if the detergent is incorporated in an amount of more than 20.0 wt. %, the improved thermal oxidation durability and detergency corresponding to the increased amount are not expected. The use of the salicylate detergent in such a large amount is not economical.

Ashless Detergent

Into the lubricating oil composition, an ashless dispersant is further incorporated in an amount of 0.1 to 10.0 wt. %, preferably 0.5 to 10.0 wt. %, and most preferably 1.0 to 5.0 wt %, based on the total amount of the lubricating oil composition of the present invention. Generally in the dispersant, a hydrocarbon oil which has been used in preparing the ashless dispersant is contained in a small amount, and hence the above-mentioned amount for the dispersant includes not only the active component but also the remaining hydrocarbon oil. In the case where succinimide is employed as the dispersant, the amount of the succinimide may be 0.001 to 0.15 wt. %, preferably 0.008 to 0.15 wt. %, in terms of the nitrogen content.

Examples of the ashless dispersants include mono-imides or bis-imides modified with organic acids. Preferred is an ashless succinimide dispersant. The succinimide dispersant can be prepared by the steps of, for example, conducting a reaction at 100 to 200°C between maleic anhydride and a polybutene or chlorinated polybutene having a molecular weight of 800 to 8,000 to give a polybutenylsuccinic anhydride, and reacting the obtained anhydride with a polyamine. Examples of the polyamines include diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, and hexaethyleneheptamine. The succinimide dispersant is preferably borated, and the preferable borated dispersant can be prepared, for example, by a reaction between the above-mentioned product (i.e., polybutenylsuccinimide) and boric acid (or a boric acid derivative).

If the content of the ashless dispersant in the lubricating oil composition is less than 0.1 wt. %, the oil composition exhibits poor stability against water-contamination and the sludge is not dispersed well. On the other hand, if the dispersant is incorporated in an amount of more than 10.0 wt. %, the oil composition sometimes exhibits poor thermal stability.

Zinc Dialkyldithiophosphate

Furthermore in the lubricating oil composition, a zinc dialkyldithiophosphate (ZnDTP) is incorporated in an amount of 0.1 to 2.0 wt. %, preferably 0.1 to 1.5 wt. %, and most preferably 0.3 to 1.0 wt %, based on the total amount of the lubricating oil composition of the present invention. Generally in ZnDTP, a hydrocarbon oil, which has been used in preparing the ZnDTP, is contained in a small amount, and hence the above-mentioned amount for the ZnDTP includes not only the active component but also the remaining hydrocarbon oil. The amount of ZnDTP may be 0.001 to 0.15 wt. %, preferably 0.001 to 0.11 wt. %, in terms of the phosphorus content.

The alkyl group of zinc dialkyldithiophosphate may be, for example, a straight or branched primary, secondary or tertiary alkyl group of 2 to 18 carbon atoms. Examples of the alkyl groups include ethyl, propyl, isopropyl, butyl, pentyl, hexyl, heptyl, octyl, decyl, dodecyl, and octadecyl.

If the content of ZnDTP in the lubricating oil composition is less than 0.1 wt. %, the oil composition can not have enough oxidization durability and detergency. On the other hand, even if ZnDTP is incorporated in an amount of more than 2.0 wt. %, the improved thermal oxidation durability and detergency corresponding to the increased amount is not expected.

Nonmetallic Oxidation Inhibitor

Into the lubricating oil composition, a nonmetallic oxidation inhibitor is furthermore incorporated in an amount of 0.05 to 2.0 wt. %, preferably 0.1 to 1.0 wt. %, and most preferably 0.3 to 1.0 wt. %, based on the total amount of the composition. If the amount is less than 0.05 wt. %, the oxidation inhibitor cannot satisfactorily prevent the oxidation. Even if the oil composition contains the oxidation inhibitor in an amount of more than 2.0 wt. %, the improved thermal oxidation durability and detergency is not expected.

Preferably, the nonmetallic oxidation inhibitor is a phenolic oxidation inhibitor. Examples of the phenolic oxidation inhibitors include hindered phenols such as 2,6-di-t-butyl-p-cresol, 4,4'methylenebis-(2,6-di-t-butylphenol), 4,4'-thio-bis(2-methyl-6-t-butylphenol), 2'-thiodiethylenebis[3(3,5-di-t-butyl-4-hydroxyphenyl) propionate], and iso-octyl 3(3,5-di-t-butyl-4-hydroxyphenyl)propionate. These inhibitors may be used singly or in combination. The phenolic oxidation inhibitor may also be used in combination with other nonmetallic oxidation inhibitors. In addition to phenolic oxidation inhibitors, oxidation inhibitors of amine type, dithiocarbamate type, or sulfuric compound type are also employable.

The Lubricating Oil Composition

The lubricating oil composition of the present invention is useful for imparting improved thermal oxidation durability and detergency of an internal combustion engine, particularly trunk piston engines such as land generators and ships. Such a lubricating oil composition comprises a base oil of lubricating viscosity and an effective amount of the above compounds.

In its broadest embodiment, the lubricating oil composition would contain:

(A) a base oil of lubricating viscosity having a kinematic viscosity of 22 to 300 mm^2à/s at 40°C,

(B) 1.0 to 20.0 wt. % of an overbased alkyloxybenzenesulfonate detergent,

(C) 1.0 to 20.0 wt. % of a neutral or basic salicylate detergent,

(D) 0.1 to 10.0 wt. % of an ashless dispersant,

(E) 0.1 to 2.0 wt. % of a zinc dialkyldithiophosphate, and

(F) 0.05 to 2.0 wt. % of a nonmetallic oxidation inhibitor.

In another embodiment, the lubricating oil composition would contain:

(A) a base oil having a kinematic viscosity of 22 to 300 mm^2à/s at 40°C,

(B) 0.1 to 2.5 wt. % in terms of calcium content of an overbased calcium alkyloxybenzenesulfonate detergent,

(C) 0.05 to 2.0 wt. % in terms of calcium content of a neutral or basic calcium salicylate detergent,

(D) 0.001 to 0.15 wt. % in terms of nitrogen content of an ashless succinimide dispersant,

(E) 0.001 to 0.15 wt. % in terms of phosphorus content of a zinc dialkyldithiophosphate, and

(F) 0.05 to 2.0 wt. % in terms of content of its phenolic oxidation inhibitor.

The lubricating oil composition of the invention can be prepared by successively or simultaneously adding the additive components to a base oil, or by beforehand preparing the additive composition as a concentrate and then mixing it with a base oil.

In a further embodiment, a lubricating oil composition is produced by blending a mixture of the above components. The lubricating oil composition produced by that method might have a slightly different composition than the initial mixture, because the components may interact. The components can be blended in any order and can be blended as combinations of components.

Other additives which may be present in the present lubricating oil composition include, but are not limited to, rust inhibitors, foam inhibitors, corrosion inhibitors, metal-deactivators, pour point depressants, anti-oxidants, and a variety of well-known additives.

Additive Concentrates

Additive concentrates are also included within the scope of the present invention. The concentrate of the present invention usually include the product produced by blending:

(A) 1.0 to 30 wt % of a compatible organic liquid diluent

(B) 5.0 to 90.0 wt. % of an overbased alkyloxybenzenesulfonate detergent,

(C) 5.0 to 90.0 wt. % of a neutral or basic salicylate detergent,

(D) 0.5 to 50.0 wt. % of an ashless dispersant,

(E) 0.5 to 15.0 wt. % of a zinc dialkyldithiophosphate, and

(F) 0.1 to 15.0 wt. % of a nonmetallic oxidation inhibitor.

In a further embodiment, the concentrate of the present invention may comprise the product produced by blending:

(A) 1.0 to 30 wt. % of a compatible organic liquid diluent,

(B) 0.5 to 12.0 wt. % in terms of calcium content of an overbased calcium alkyloxybenzenesulfonate detergent,

(C) 0.3 to 10.0 wt. % in terms of calcium content of a neutral or basic calcium salicylate detergent,

(D) 0.005 to 1.0 wt. % in terms of nitrogen content of an ashless succinimide dispersant,

(E) 0.005 to 1.1 wt. % in terms of phosphorus content of a zinc dialkyldithiophosphate, and

(F) 0.1 to 15.0 wt. % in terms of content of a phenolic oxidation inhibitor.

The concentrates contain sufficient organic liquid diluent to make them easy to handle during shipping and storage.

Suitable organic diluents which can be used include for example, solvent refined 100N, i.e., Cit-Con 100N, and hydrotreated 100N, i.e., Chevron 100N, and the like. The organic diluent preferably has a viscosity of about from 1.0 to 20 cSt at 100°C.

The components of the additive concentrate can be blended in any order and can be blended as combinations of components. The concentrate produced by blending the above components might be a slightly different composition than the initial mixture because the components may interact.

EXAMPLES

The invention will be further illustrated by the following examples, which set forth particularly advantageous specific embodiments. While the Examples are provided to illustrate the present invention, they are not intended to limit it.

Examples 1-8

In each of Examples 1-8, a lubricating oil composition for a diesel internal combustion engine [SAE viscosity grade: 40, TBN:30 (measured by D2896)] was prepared using the following components. The components employed are set forth in Table 1 (in terms of wt. %).

(1) Overbased alkyloxybenzenesulfonate detergent
(A) Calcium phenoxysulfonate [TBN: 300, calcium content: 12.3 wt.%]

(2) Neutral or basic salicylate detergent

(A) Calcium salicylate [TBN: 230, calcium content: 8.2 wt. %]

(B) Calcium oxybenzene carboxylate-phenate sulfide complex [TBN: 270, calcium content: 9.6 wt. %]

(3) Ashless dispersant

(A) Succinimide [nitrogen content: 0.66 wt. %]

(B) Succinimide borate [nitrogen content: 1.5 wt. %, boron content: 0.5 wt. %]

(4) Zinc dialkyldithiophosphate (ZnDTP)
Zinc dialkyldithiophosphate having an alkyl group of eight carbon atoms [phosphorus content: 7.4 wt. %]

(5) Nonmetallic oxidation inhibitor
Propionic ester of hindered phenol: iso-octyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate

(6) Base oil

(A) Paraffinic base oil of 500 NL [kinematic viscosity at 40°C: 100 mm^2à/s]

(B) Paraffinic base oil of bright stock 150 [Kinematic viscosity at 40°C: 480 mm^2à/s]

(7) Calcium phenate [TBN: 255, calcium content: 9.2 wt. %]

(8) Calcium sulfonate [TBN: 300, calcium content: 11.8 wt. %]

The characteristics of each oil composition were evaluated by the following tests, and the results are set forth in Table 1.

1) ISOT (165.5°C/72 hours) test

1-1) Viscosity increase: Each value shown in Table 1 is a ratio of viscosity at 40°C (after the test/before the test). The lower the number the better the results.

1-2) TAN increase (Total Acid Number, measured by D664): Each value shown in Table 1 is a difference of TAN after the test to that before. The lower the number the better the results.

1-3) TBN retention (Total Base Number, measured by HCL): Each value shown in Table 1 is a percentage of TBN after the test based on that before. The higher the number the better the results.

2) Hot Tube Test (325°C/16 hours).

Each value shown in Table 1 indicates the degree of cleanliness. The value of a clean test tube is set at 10. Therefore, the higher the number the better the results.

Table 1 - Examples

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8
(1)	6.97	6.97	6.97	6.97	6.97	4.96	6.97	6.97
(2A)	-	3.91	3.91	3.91	3.91	6.52	3.91	3.91
(2B)	3.33	-	-	-	-	-	-	-
(7)	-	-	-	-	-	-	-	-
(8)	-	-	-	-	-	-	-	-
(3A)	-	-	2.0	-	-	-	-	-
(3B)	2.0	2.0	-	1.5	2.0	2.0	2.0	2.0
(4)	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67
(5)	0.3	0.3	0.3	0.3	0.1	0.3	0.3*	0.3**
(6A)	65.0	64.7	64.7	64.9	64.7	64.1	64.7	64.7
(6B)	21.7	21.5	21.5	21.7	21.6	21.4	21.5	21.5
Results of the ISOT Test								
1-1)	1.16	1.09	1.11	1.12	1.12	1.16	1.18	1.24
1-2)	1.15	0.85	0.97	0.98	1.11	1.20	1.25	1.45
1-3)	38.3	45.8	42.8	42.8	40.0	38.5	35.1	34.2
Results of the Hot Tube Test								
2)	6.0	7.0	6.5	6.5	6.5	7.0	6.0	6.0

*4,4' - Methylene bis(2,6-di-t-butylphenol)

**Dialkyldiphenylamine

Comparison Examples 1-5

In each of Comparison Examples 1-5, a lubricating oil composition for diesel internal combustion engine [SAE viscosity grade: 40, TBN:30 (measured by D2896)] was prepared from the above-described components, unless otherwise noted. The components employed for each example are set forth in Table 2 (in terms of wt. %).

The characteristics of each oil composition for comparison were evaluated in the same manner as described above, and the results are set forth in Table 2.

Table 2 -

Comparative Examples					
	Com. Ex. 1	Com. Ex. 2	Com. Ex 3	Com Ex. 4	Com. Ex. 5
(1)	6.97	6.97	9.97	-	6.97
(2A)	-	-	-	13.0	3.91
(2B)	-	-	-	-	-
(7)	3.51	-	-	-	-
(8)	-	2.0	-	-	-
(3A)	-	-	-	-	-
(3B)	2.0	2.0	2.0	2.0	2.0
(4)	0.67	0.67	0.67	0.67	0.67
(5)	0.3	0.3	0.3	0.3	-
(6A)	65.0	66.1	65.2	63.0	64.8
(6B)	21.6	22.0	21.8	21.0	21.6
Results of the ISOT Test					
1-1)	1.26	1.34	1.15	1.25	1.26
1-2)	1.59	1.98	1.10	1.49	1.89
1-3)	30.0	29.5	38.3	34.5	31.8
Results of the Hot Tube Test					
2)	4.5	3.0	4.5	7.0	6.0

In Table 1, each lubricating oil composition of the present invention exhibits relatively small increases of both viscosity and TAN, and satisfactory TBN retention in the ISOT Test. Further in Table 1, the Hot Tube Test shows that the lubricating oil compositions of the present invention show low deposits because thermal oxidation degradation of the lubricating oil is low. The lubricating oil compositions of the comparative examples shown in Table 2 are inferior to those of the present invention in the ISOT Test (increases of viscosity, TAN, and TBN retention) and/or the Hot Tube Test (deposits due to oxidation of lubricating oil).

In order to achieve acceptable results in both the ISOT Test and Hot Tube Test, the lubricating oil composition of the present invention is required. Examples 1-8 demonstrate that a specific nonmetallic oxidation inhibitor, particularly a phenolic oxidation inhibitor, more specifically iso-octyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, contributes to the unexpected improvement in the properties measured by the ISOT Test and Hot Tube Test. The use of other nonmetallic oxidation inhibitors (Examples 7 and 8) provided an improvement in Hot Tube Test, but the results of the ISOT Test were inferior. Moreover, the improved properties are observed when iso-octyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate is used in combination with both an overbased alkyloxybenzenesulfonate and a neutral or basic salicylate detergent in the lubricating oil composition (Examples 1-6). The results of the ISOT Test and Hot Tube Test are inferior when iso-octyl 3-(3, 5-di-t-butyl-4-hydroxyphenyl) -propionate is used with either an overbased alkyloxybenzenesulfonate or a neutral or basic salicylate detergent alone (Comparative Examples 1-4). Having only an overbased alkyloxybenzenesulfonate and a neutral or basic salicylate detergent without the non-metallic oxidation inhibitor of the present invention in the lubricating oil composition also yields inferior results (Comparative Example 5). From these results, it is apparent to a skilled artisan that the combination of an overbased alkyloxybenzenesulfonate, a neutral or basic salicylate detergent, and a specific nonmetallic oxidation inhibitor, particularly a phenolic oxidation inhibitor, more specifically iso-octyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, contributes to the unexpected improvement in the properties measured by the ISOT Test and Hot Tube Test.

The lubricating oil composition of the present invention has enough stability against thermal oxidation and enough detergency at an elevated temperature to comply with the severe operating conditions required for modern diesel engines, particularly trunk piston engines such as land generators and ships. Therefore, if the lubricating oil composition of the present invention is employed for the engines operating continuously for long periods of time under severe conditions, it can reduce troublesome problems such as viscosity increase and consumption of the lubricating oil; production of black sludge derived from impurities and combustion residues of the fuel and the lubricating oil; accumulation of sludge on piston land, groove and piston undercrown; and friction wear of piston ring and cylinder liner.

While the present invention has been described with reference to specific embodiments, this application is intended to cover those various changes and substitutions that may be made by those skilled in the art without departing from the spirit and scope of the appended claims.

Claims

1. A lubricating oil composition comprising the product produced by blending:

   (A) a base oil of lubricating viscosity having a kinematic viscosity of 22 to 300 mm^2/s at 40°C,

   (B) 1.0 to 20.0 wt. % of an overbased alkyloxybenzenesulfonate detergent,

   (C) 1.0 to 20.0 wt. % of a neutral or basic salicylate detergent,

   (D) 0.1 to 10.0 wt. % of an ashless dispersant,

   (E) 0.1 to 2.0 wt. % of a zinc dialkyldithiophosphate, and

   (F) 0.05 to 2.0 wt. % of a nonmetallic oxidation inhibitor.

2. A lubricating oil composition according to Claim 1, wherein

   (A) 2.0 to 10.0 wt. % of said overbased alkyloxybenzenesulfonate detergent is present,

   (B) 1.0 to 10.0 wt. % of said neutral or basic salicylate detergent is present,

   (C) 0.5 to 10.0 wt. % of said ashless dispersant is present,

   (D) 0.1 to 1.5 wt. % of said zinc dialkyldithiophosphate is present, and

   (E) 0.1 to 1.0 wt. % said nonmetallic oxidation inhibitor is present.

3. A lubricating oil composition according to Claim 1, wherein

   (A) 4.0 to 8.0 wt. % of said overbased alkyloxybenzenesulfonate detergent is present,

   (B) 2.0 to 8.0 wt. % of said neutral or basic salicylate detergent is present,

   (C) 1.0 to 5.0 wt. % of said ashless dispersant is present,

   (D) 0.3 to 1.0 wt. % of said zinc dialkyldithiophosphate is present, and

   (E) 0.3 to 1.0 wt. % of said nonmetallic oxidation inhibitor is present.

4. The lubricating oil composition according to Claim 1, wherein said overbased alkyloxybenzenesulfonate detergent has a TBN of at least 200.

5. The lubricating oil composition according to Claim 1, wherein said overbased alkyloxybenzenesulfonate detergent is a calcium salt of an overbased alkyloxybenzenesulfonic acid having a TBN of at least 200.

6. The lubricating oil composition according to Claim 1, wherein said neutral or basic salicylate detergent has a TBN of at least 60.

7. The lubricating oil composition according to Claim 1, wherein said ashless dispersant is succinimide which has a polybutenyl group having a molecular weight of 800 to 8,000.

8. The lubricating oil composition according to Claim 7, wherein said ashless dispersant is a borate of succinimide.

9. The lubricating oil composition according to Claim 1, wherein said nonmetallic oxidation inhibitor is a phenol compound.

10. The lubricating oil composition according to Claim 9, wherein said nonmetallic oxidation inhibitor is an ester of a phenol compound.

11. The lubricating oil composition according to Claim 10, wherein said ester of a phenol compound is iso-octyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate.

12. A lubricating oil composition comprising the product produced by blending:

(A) a base oil having a kinematic viscosity of 22 to 300 mm^2à/s at 40°C,

(B) 0.1 to 2.5 wt. % in terms of calcium content of an overbased calcium alkyloxybenzenesulfonate detergent,

(C) 0.05 to 2.0 wt. % in terms of calcium content of a neutral or basic calcium salicylate detergent,

(D) 0.001 to 0.15 wt. % in terms of nitrogen content of an ashless succinimide dispersant,

(E) 0.001 to 0.15 wt. % in terms of phosphorus content of a zinc dialkyldithiophosphate, and

(F) 0.05 to 2.0 wt. % in terms of content of its phenolic oxidation inhibitor.

13. The lubricating oil composition according to Claim 12, wherein said overbased calcium alkyloxybenzenesulfonate detergent has a TBN of at least 200.

14. The lubricating oil composition according to Claim 12, wherein said neutral or basic calcium salicylate detergent has a TBN of at least 60.

15. The lubricating oil composition according to Claim 12, wherein said ashless succinimide dispersant is a borate of succinimide which has a polybutenyl group having a molecular weight of 800 to 8,000.

16. A concentrate comprising the product produced by blending:

(G) 1.0 to 30 wt % of a compatible organic liquid diluent

(H) 5.0 to 90.0 wt. % of an overbased alkyloxybenzenesulfonate detergent,

(I) 5.0 to 90.0 wt. % of a neutral or basic salicylate detergent,

(J) 0.5 to 50.0 wt. % of an ashless dispersant,

(K) 0.5 to 15.0 wt. % of a zinc dialkyldithiophosphate, and

(L) 0.1 to 15.0 wt. % of a nonmetallic oxidation inhibitor.

17. A concentrate according to Claim 16, wherein said overbased alkyloxybenzenesulfonate detergent is a calcium salt of an overbased alkyloxybenzenesulfonic acid having a TBN of at least 200.

18. A concentrate according to Claim 16, wherein said neutral or basic salicylate detergent has a TBN of at least 60.

19. A concentrate according to Claim 16, wherein said ashless dispersant is a borate of succinimide which has a polybutenyl group having a molecular weight of 800 to 8,000.

20. A concentrate comprising the product produced by blending:

(A) 1 to 30 wt % of a compatible organic liquid,

(B) 0.5 to 12.0 wt. % in terms of calcium content of an overbased calcium alkyloxybenzenesulfonate,

(C) 0.3 to 10.0 wt. % in terms of calcium content of a neutral or basic calcium salicylate detergent,

(D) 0.005 to 1.0 wt. % in terms of nitrogen content of an ashless succinimide dispersant,

(E) 0.005 to 1.1 wt. % in terms of phosphorus content of a zinc dialkyldithiophosphate, and

(F) 0.1 to 15.0 wt. % in terms of content of its phenolic oxidation inhibitor.

21. A concentrate according to Claim 20, wherein said overbased calcium alkyloxybenzene-sulfonate detergent has a TBN of at least 200.

22. A concentrate according to Claim 20, wherein said neutral or basic calcium salicylate detergent has a TBN of at least 60.

23. A concentrate according to Claim 20, wherein said ashless succinimide dispersant is a borate of succinic imide which has a polybutenyl group having a molecular weight of 800 to 8,000.

24. A method of improving the thermal oxidation durability and detergency of an internal combustion engine, said method comprising lubricating said internal combustion engine with a lubricating oil composition according to Claim 1.

25. A method of improving the thermal oxidation durability of an internal combustion engine according to Claim 24, wherein said internal combustion engine is a trunk piston engine.

26. A method for producing a lubricating oil composition comprising blending the following components together:

(A) a base oil of lubricating viscosity having a kinematic viscosity of 22 to 300 mm^2a/s at 40°C,

(B) 1.0 to 20.0 wt. % of an overbased alkyloxybenzenesulfonate detergent,

(C) 1.0 to 20.0 wt. % of a neutral or basic salicylate detergent,

(D) 0.1 to 10.0 wt. % of an ashless dispersant,

(E) 0.1 to 2.0 wt. % of a zinc dialkyldithiophosphate, and

(F) 0.05 to 2.0 wt. % of a nonmetallic oxidation inhibitor.

27. A lubricating oil composition produced by the method according to Claim 26.